# Mechanical behavior of biopolymer composite coatings on plastic films by depth-sensing indentation – A nanoscale study

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Within the field of biopolymer-based systems, the development of

#### biocomposite thin films and coatings incorporating nanobuilding blocks

(NBBs) deposited on plastic films is emerging in different fields

(e.g., optical devices, displays and screens, and food packaging...)

## The properties of the nanocomposite layer depend largely on the interaction

between the matrix and the filler

#### Raise the need of fast and robust technique that enables the quantitative

description of the mechanical performance on a nanoscale.





## **Double-Layered system**

Pullulan used as a biopolymer phase

- **Fully amorphous organization**  $\Rightarrow$  high flexibility, good optical properties
  - **Uncharged**  $\Rightarrow$  interact with polar counterparts bearing a positive,

negative, or neutral charge through ion-dipole and dipole-dipole interactions.

- Its aqueous solutions are stable over a broad range of pH ⇒ large use
  Polyetylene terephthalate (PET) 12 um film as a plastic substrate
- widespread used, e.g., for the manufacturing of flexible thin film cells for photovoltaic panels and pharmaceutical packaging applications.





# 🔏 Our Subject

#### Colloidal silica (CS) and cellulose nanocrystals (CNCs)

used as representative spherical and rod-like NBBs

#### - widespread use as nanoscale reinforcing fillers

papermaking, packaging, construction, electronics, photography, metal casting, paints, beverages, polishes ...

 CNCs interesting for renewable nature, anisotropic shape, remarkable mechanical properties, good biocompatibility, tailorable surface chemistry, and excellent optical properties





# A Problems and performances

## Lack of affinity at the interface between the two phases

(biopolymer network and nanofiller)

## Due to:

- Chemical heterogeneity
- Thermodynamic incompatibility
- Physical hindrance
- Molecular arrangements
- etc.

## Generate problems:

- Interfacial de-bonding
- Phase segregation
- Filler aggregation
- Filler re-agglomeration
- Increase in void content





# A Problems and performances

### Problems affect the material's performance:

Permeability of gases and vapors (increase in the diffusion coefficient) Mechanical integrity (crack formation and propagation) Optical properties (scattering centers) Dielectric performance (charge accumulation) Thermal stability

How to test the problems related observables?

We need info about the

Mechanical response at the Nanoscale





#### Why Indentation?

- Instrumented, controlled and reproducible
- Well known and used technique (mostly metals and ceramics)

## Why Nano?

- To prevent any potential influence of the supporting substrate
  - For scale reason
  - Both local than average behaviour can be analyzed

## It gives the possibility to:

- Discriminate between the contribution of substrate and coating
- Find clear evidence of the reinforcing effect of NBBs on a local scale
  - Identify of nanofiller types in a reliable fashion.





Berkovich indenter

Oliver and Pharr Method

Elastic Modulus







A Better Measure



#### Pullulan powder (PF-20 grade, Mn 200 kDa)

from Hayashibara Biochemical Laboratories Inc. (Okayama, Japan)

Colloidal Silica Nanoparticle water dispersions AkzoNobel (Amsterdam, Netherlands) CS15/500 Bindzil15/500 particle size: 5 nm; polydispersity index: 22.5%; dry matter: 15 wt%; specific surface area: 500 m2 g1 at pH =10.0 CS15/750 Bindzil 15/750 particle size: 4 nm; polydispersity index: 22.4%; dry matter: 15 wt%; specific surface area: 750 m2 g1 at pH = 10.5 CS2034 Bindzil 2034 DI particle size: 15 nm; polydispersity index: 27.3%; dry matter: 34 wt%; specific surface area: 200 m2 g1 at pH = 2.8

Cellulose nanocrystals (CNCs) obtained by acid catalyzed hydrolysis in our laboratory

#### **One-side corona-treated PET A-410**

(JBF RAK LLC, Ras Al Khaimah, United Arab Emirates)  $12.0 \pm 0.5$  um thick Kindly supplied by Metalvuoto spa (Roncello, Italy).





**Sample P reference:** pristine pullulan solution (10.0 wt% wet basis)

#### Samples P-CS15/500, P-CS15/750, and P-CS2034):

Pullulan colloidal silica dispersions Raw CS water dispersion added to the pullulan solution, final CS concentration: 3 wt% wet basis on the total weight, 30 wt% with respect to dry pullulan

#### Sample P-CNC:

Prepared CNC water dispersion added to the pullulan solution final CNC concentration:

0.3 wt% wet basis on the total weight, 3.6 wt% with respect to dry pullulan

Mixing for 24 h at 500 rpm at 25 C all the formulations left to rest for an additional 24 h before coating deposition.





#### On the corona-treated side of PET

Automatic applicator following: ASTM D823-07, Practice C Constant speed: 150 mm/min

**Mayer rods with selected engraved patterns were used** to reset any possible difference arising from the different concentrations of the water dispersions

#### Solvent evaporation: 2x type B infra-red (IR) lamps 1440W Constant ,perpendicular flux of air $25.0 \pm 0.3$ C 2 min at distance 40 cm

Final dry thickness: 3.5 um for all five dry coatings.

Stored in a polycarbonate vacuum (0.06 MPa) desiccator under dry conditions for an additional two weeks before analyses.





#### PB1000 Nanovea Mechanical Tester with 400mN Nano Module

Very low target loads [40 µN-400mN]

Force applied with a piezo driver while monitoring the load with an independent load cell and fine recording the position of the indenter inside the material with an independent capacitive depth sensor.

A multichannel 24-bit acquisition card controlled every sensor and actuator.

The samples were glued on sample holders and let dry for 30 min before testing in the environment enclosure of the instrument at 23 C and 40% RH.

**10% Rule** loads in order to have indentation with depth inside 10% total coating thickness





#### To demonstrate the absence of any interference of the PET substrate

#### First Step:

H [Mpa] of the PET-coated surfaces (both the coating surface and the PET surface) H [Mpa] of the uncoated PET

maximum load 0.2 mN; indentation depth 120 nm; loading/unloading rate 800 uN/min



Results are expressed as mean values and standard deviation.

<sup>a-c</sup>Different superscripts within a group (i.e., within each parameter for each step) refer to a statistically significant difference (p < .05).





#### To demonstrate the absence of any interference of the PET substrate

#### Second step: on P-CNC

Perform the same test as above but at different maximum loadings: 0.1 mN, 0.2 mN, 0.3 mN, 0.5 mN, 0.7 mN, 1.0 mN, and 1.2 mN





The indentation test is able to discriminate between plastic substrate and coating

For indentation loads <0.2 mN and penetration depths <155 nm The nanomechanical behavior of the coating is independent from the substrate.

Above those values, the influence of the substrate starts to affect the overall measurement, leading to an overestimation of the hardness of the coating.





## **Mechanical Properties and Distribution Effects**

## Set up 1: P, P-CS15/500, P-CS15/750 Matrix of 10x8 indentations Spacing of 0.3 μm Depth control at the maximum depth of 40 nm

## Set up 2: P, P-CNC, P-CS2034

because of the larger average size of the fillers: Matrix of 6x6 indentations Spacing of 1  $\mu$ m Load control at a maximum load of 200  $\mu$ N.

Indentations were reciprocally independent





## **Mechanical Properties and Distribution Effects**









## **Mechanical Properties and Distribution Effects**



Fig. 4. Three-dimensional images of hardness (*H*, MPa) distribution on representative portions (2.70 × 2.10  $\mu$ m<sup>2</sup>) of the coating surface of samples P (left), P-CS<sub>15/500</sub> (center), and P-CS<sub>15/750</sub> (right).

- 1) The addition of colloidal silica has a significant reinforcing effect on the matrix
- 2) P-CS15/500 (center) has a more homogeneous distribution of the nanoparticles compared with sample P-CS15/750 (right) Apparently, the addition of smaller particles with higher surface area drove the formation of larger domains separated from the main biopolymer matrix.
- 3) The reinforcing effect of CS nanoparticles observed in this work is within the same order of magnitude as the values recorded for both thermoset (e.g., epoxy and polyacrylates) and thermoplastic matrices.







## **Mechanical Properties and Shape Effects**

#### Rod Like CNC vs Spherical CS2340

Addition of spherical nanoparticles (sample P-CS2034) has a greater effect on the surface hardness compared to the cellulose nanowhiskers (sample P-CNC)

# Differences in distributions of the particles clearly visible

| Coating sample | E (GPa)                   | H (MPa)                     |
|----------------|---------------------------|-----------------------------|
| Step 2         | 5 S. S. 1999              |                             |
| Р              | $6.91 \pm 0.73^{a}$       | 290.47 ± 29.69 <sup>A</sup> |
| P-CNC          | 7.73 ± 1.51 <sup>b</sup>  | 321.36 ± 43.26 <sup>B</sup> |
| P-CS2034       | 7.33 ± 0.82 <sup>ab</sup> | 353.50 ± 83.52 <sup>C</sup> |





## **Mechanical Properties and Shape Effects**

"two-color" CS pattern stems from a nonuniform distribution local aggregation and clustered silica domains

CS15/500 and CS15/750 are anionic nanoparticles (i.e., the net negative charge prevents cluster formation

CS2034 are zero-charge nanoparticles (i.e., particle aggregation by, e.g., hydrogen bonding is favored).





## Creep

C value relies more on a mean distribution of the nanoparticles at a microscale, rather than on local gradients

Addition of CS nanoparticles, also if not homogeneously dispersed, gives a more cohesive surface

The solvent removal during the preparation of thin films and coatings (as in this work) promotes the formation of aggregates or agglomerates with a very small accessible surface area, which in turn would affect the interaction at the interface with the main polymer matrix

And with the Nano Indentation we can see and measure all these properties, behaviour and helps in finding the reason of the problems





## Conclusions

In this work, for the first time we used nanoindentation to gather nanomechanical information of biopolymer nanocomposite thin coatings deposited on a plastic film being able to discriminate between different kind of nano filler

- 1) the substrate's mechanical properties do not affect the mechanical characterization of the coating if a suitable instrumental setup is used
- 2) the addition of NBBs was successfully discriminated from the bare biopolymer and new nanomechanical features E, H and Creep were described.
- 3) The impact of NBBs geometry on the nanomechanical performance of the final nanocomposite coatings was also addressed in light of some surface chemistry considerations. This has revealed unexpected behaviors for round-shaped NBBs and rod like NBBs

We hope this work may represent a step forward to expand the use of nanoindentation for the special application on bio nanocomposite coatings deposited on relatively thin and flexible substrates



# Thank you for your kind attention

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